ROGERS

Determination of Oxygen Consumed And Nitrogen as Nitrates

CHEMISTRY

M. S.

1909

DETERMINATION OF OXYGEN CONSUMED AND NITROGEN AS NITRATES

BY

JEROME STANLEY ROGERS

B S. Syracuse University, 1907

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

MASTER OF SCIENCE

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1909

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

July 18 1908

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JEROME STANLEY ROGERS, B. S., SYRACUSE UNIVERSITY, 1907.

ENTITLED THE DETERMINATION OF OXYGEN CONSUMED AND OF NITROGEN AS NITRATES.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

Edward Bartow
In Charge of Major Work

Wm A. Noyes
Head of Department

Recommendation concurred in:

Committee
on
Final Examination

UNIVERSITY OF ILLINOIS

July 18, 1908

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Jerome Stanley Rogers, B. S., Syracuse University, 1907.

ENTITLED The Determination of Oxygen Consumed and of Nitrogen as Nitrates.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Master of Science

Edward Bartow.
Instructor in Charge.

APPROVED: Wm A. Noyes.

HEAD OF DEPARTMENT OF Chemistry.

THE DETERMINATION OF OXYGEN CONSUMED AND OF NITROGEN AS NITRATES.

PART I.

OXYGEN CONSUMED.

PART II.

NITROGEN AS NITRATE.

INTRODUCTION.

In determining the potability of the natural waters of Illinois, the tests of "Oxygen Consumed" and Nitrates" hold an important place. Several methods have been recommended for making each of these determinations. Because of the variation in the results obtained by the various methods, we planned to try to determine the reason for the variations and to attempt to decide which was best from the standpoint of accuracy and ease of manipulation.

PART I. OXYGEN CONSUMED. The determination depends upon the decolorization of permanganate of potassium. Many modifications, depending mainly on the temperature and time of digestion, have been tried. A very good resume of the status of this test has been given by J. B. Weems* in an article read before the Iowa Engineering Society at Davenport, entitled, "The Evolution of the Oxygen Absorption Test in Water Analysis". This article gives a very good review of the different methods which have been used. Forchammer* first proposed the use of potassium permanganate to determine the unoxidized organic matter. His method was modified to some extent by Schrotter, Monnier, and Hervier. Dr. Woods* proposed heating

---

*Proc. Iowa Eng. Soc., Jan. 1901, p. 20.

*Fres. Zeit. of Anal. Chem. I. p. 246.

*Jr. Chem. Soc. (2) I. p. 62 abs (also)

*Fres. Zeit. f. Anal. Chem. II. p. 425.

the mixture to 60°C. before the addition of the permanganate. Miller* an English chemist, published a method in which he used potassium iodide in sulphuric acid solution to decompose the excess of potassium permanganate used in the oxidation and the iodine set free was titrated with sodium thiosulphate. The time considered necessary at ordinary temperatures was three hours. Two years after the publication of Miller's method, Kubel* suggested that the water under examination, be boiled for five minutes after the permanganate had been added.

Schulze suggested that an alkaline solution be used for the titration in place of the sulphuric acid solution. Dr. C. M. Tidy* used the method of Miller and made two determinations on each sample and one on a blank at the same time. In one determination he allowed the potassium permanganate to act for one hour; in the other it was allowed to act for three hours. He did not take the temperature into consideration. The three methods which have been followed most closely up to the present day are those of Kubel, Schulze, and the Chemical Section of the American Association for the Advancement of Science.

The Kubel method, as stated by Weems, is as follows;

---

*Fres. Zeit. f. Anal. Chem. IV. p. 462

*Fres. f. Anal. Chem. VI. 252.

*Jr. f. prak. Chem. 99, p. 337 abs.

*Jr. Chem. Soc. 1879, p. 66 abs.

*Fres. Zeit. f. Anal. Chem. XIX. p. 492.

"100 c.c. of the water is placed in a 300 c.c. flask and to this then is added 5 c.c. of dilute H_2SO_4 (1:3) and a quantity of N/100 $KMnO_4$ solution. The quantity of the $KMnO_4$ solution added should be such that at the end of the reaction the solution should have the characteristic color of this substance. The contents of the flask are boiled for ten minutes and then ten c.c. of standard oxalic acid solution are added, and the solution is titrated to color with standard $KMnO_4$."

"Schulze Method. 100 c.c. of the water to be examined is placed in a 300 c.c. flask, and then is added 1/2 c.c. NaOH (1:2). Ten c.c. of standard $KMnO_4$ is added and the mixture boiled for about 10 minutes. It is then allowed to cool to 50° or 60° C., and, after acidifying with 5 c.c. of H_2SO_4 (1:3), 10 c.c. of oxalic acid are added and the solution is titrated to color as in the Kubel method."

The method recommended by the Chemical Section of the American Association for the Advancement of Science* is as follows:

"To 200 c.c. of the water to be examined in a 400 c.c. flask, add 10 c.c. of dilute H_2SO_4 (1:3) and such measured quantity of $KMnO_4$ as will give a persistant color; boil ten minutes, add, if necessary, more $KMnO_4$ in measured quantities so as to maintain the color; remove the flask from the lamp, add 10 c.c. of oxalic acid solution, or more if required, to destroy the color caused by the excess of the $KMnO_4$, and then add $KMnO_4$ drop by drop till a faint pink tint appears. From the total quantity of the $KMnO_4$ used deduct the equivalent of the oxalic acid used, and from the remainder calculate the milligrams of oxygen consumed by the oxidizable organic

---

*Water Supply, Mason. 406.

matter in the water."

The method of Dr. Smart, which is the same as the above except that casseroles are used instead of flasks, is recommended by Mason*.

---

*Mason's Water Supply, p. 406.

The American Public Health Association, seeing the great number of methods which were in use, felt the need of a 'Standard' method which should be used by the chemists in the various laboratories. If a standard method were followed in the different laboratories the results obtained in different places would be of such a nature that they could readily be compared.

In 1905 the report of the committee on "Standard Methods of Water Analysis", was published. In this is given what are considered to be the best or 'standard' methods used in the different determinations, and it recommended that they be adopted. Two methods recommended for oxygen consumed * are as follows:

---

*Standard Methods of Water Analysis. p. 26.

---

100 c.c. of the water to be examined is measured into a flask, 10 c.c. of dilute H_2SO_4 solution and 10 c.c. of standard $KMnO_4$ solution added. The flask is then placed in a bath of boiling water in which the water is deep enough so that it stands at a higher level than the solution in the flask. The digestion is continued for exactly half an hour. Then 10 c.c. of standard oxalic acid (or ammonium oxalate) solution is added, and the whole is titrated to a color with standard $KMnO_4$. For each c.c. of $KMnO_4$ in excess of the oxalic acid there is present ,0001 gram of oxygen absorbed.

The second method, which is mostly used in England, is the same as the preceding up to the point of digestion, which is carried on at room temperature for periods of 3 minutes, 15 minutes and four hours. Some analysts make all three determinations. After digestion, 0.5 c.c. of KI solution is added to destroy the color of the $KMnO_4$, the solution is mixed and the liberated iodine titrated with sodium thiosulphate till the yellow color nearly disappears, then starch solution is added and the titration completed.

In the State Water Survey Laboratory of Illinois the thirty minute boiling method is used. This method leaves some things to be desired, and the experiments described below were undertaken to determine whether all of the oxidizable matter be oxidized in less than thirty minutes? Whether more oxidation take place by longer treatment, And whether the inorganic and organic oxidizable matter can be distinguished by different methods of treatment? There is often found in natural waters and in sewages oxidizable inorganic matter. This will be oxidized by the $KMnO_4$ and if it is desired to determine the amount of oxidizable organic matter a correction must be made.

It was thought that by direct titration with $KMnO_4$ in the cold and the immediate removal of the excess by ferrous ammonium sulphate, that it might be possible to oxidize the inorganic matter and not the organic, and thus to obtain the amount of oxygen consumed by organic matter, (see Series II) by the difference between this and the total oxygen consumed at a boiling temperature.

The Solutions used were prepared as follows:

I. Standard Potassium Permanganate Solution. Five tenths of a gram of pure $KMnO_4$ was dissolved in boiled distilled water. This solution

was boiled and filtered through glass wool. After cooling to room temperature, it was diluted to one liter with boiled distilled water. This solution was titrated against standard ferrous ammonium sulphate solution and diluted until 1 c.c. of the latter solution was equivalent to 0.997 c.c. of the $KMnO_4$. 1 c.c. of $KMnO_4$=0.0001 g. of oxygen consumed.

II. Standard Oxalic Acid Solution. Dissolved 0.7875 g. of pure crystallized substance in distilled water and diluted to one liter. This solution was titrated against the standard $KMnO_4$ solution which had been acidified with H_2SO_4, and then was diluted proportionally so that 1 c.c. of $KMnO_4$ should be equivalent to 1 c.c. of $C_2H_2O_4$.

III. Standard Ferrous Ammonium Sulphate Solution. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Four and nine tenths grams of the pure crystallized salt were dissolved in acidified distilled water and then diluted to one liter.

IV. Sulphuric Acid. The concentrated c.p. acid was used, 2 c.c. for each determination. This acid was tested and found to be free from any unoxidized matter.

The first series of analyses was made to determine the effect of different periods of digestion on the boiling water bath and in the cold. A blank determination was run on the distilled water which was being used. The determinations were made on water from the University well.

SERIES I.

c.c. of $KMnO_4$	c.c. of $C_2H_2O_4$	Excess of $KMnO_4$	Zero corrected	parts per Million	Remarks.
10	10	0.10		0.10	Distilled Water
10	10	0.10		0.10	
10	10	4.05	3.95	3.97	Digested 40 minutes in Water bath.
10	10	4.10	4.00		
10	10	3.30	3.20	3.25	Digested 30 minutes in Water bath.
10	10	3.40	3.30		
10	10	3.35	3.25	3.00	Digested 15 minutes in Water bath.
10	10	2.87	2.75		
10	10	3.35	3.25	3.15	Digested 30 minutes in Water bath. (Stopped boiling during the determination.
10	10	3.15	3.05		
10	10	3.40	3.30		
10	10	3.20	3.10		

SERIES II.

c.c. of $KMnO_4$	c.c. of $Fe(NH_4)_2(SO_4)_2$	Excess of $KMnO_4$	Zero Corrected	Parts per Million	Remarks
10	10	1.75	1.65	1.65	Digested 30 minutes cold.
10	10	1.75	1.65		
10	10	1.60	1.50	1.53	Digested 15 minutes cold.
10	10	1.65	1.55		
10	10	2.30	2.20	2.20	Digested over night cold.
10	10	2.30	2.20		

These series would indicate that with a water like the University supply the amount of oxygen consumed varies with the time of digestion, but that the reaction is more rapid at first at either of the temperatures tried. The difference between the hot and cold results are less than is allowed for well waters in the State.

As it had been noticed that characteristic filter effluents from the Illinois rivers have larger oxygen consuming capacity an attempt was made to differentiate the causes of the characteristic. Water from the Mississippi River at Quincy,,both the raw and treated, having been sent to the Laboratory, these waters were chosen for the tests.

The two waters were treated according to the thirty minute boiling method and by the immediate titration with the following results; as shown in Series III.

It will be noted that more oxygen is absorbed by the suspended matter than by the dissolved matter in both methods, and that the ratios of cold to hot in the filtered and unfiltered waters do not differ very much, being as 1 to 3.5 and as 1 to 2.9. Deducting the cold absorption from the hot absorption in the filtered water an amount only a little above 2. parts per million is obtained. If this corresponds to soluble organic matter the filtered water practically conforms to a limit of 2. parts per million. This relation it seems to us is worthy of further study.

In the determination of "Oxygen Consumed" the presence of chlorides gives an unreliable end point and high results. H. P. Cady* gives a modification for the permanganate method for the

---

*Jr. Am. Chem. Soc. 19. 575-581.

SERIES III.

c.c. of $KMnO_4$	c.c. of $C_2H_2O_4$	Excess of $KMnO_4$	Parts per Million*	Remarks.
10	10	7.45	7.35	Unfiltered Mississippi River water from Quincy, digested 30 minutes in the Water bath.
10	10	7.35	7.25	
10	10	7.35	7.25	
10	10	7.35	7.25	
10	10	7.35	7.25	
		Average	7.27	
10	10	3.20	3.10	Same as above, filtered.
10	10	3.20	3.10	
10	10	3.32	3.22	
10	10	3.61	3.51	
10	10	3.12	3.02	
		Average	3.19	
10	10	2.70	2.60	Unfiltered Mississippi River water from Quincy, titrated directly in the cold with ferrous ammonium sulphate.
10	10	2.52	2.42	
10	10	2.56	2.46	
10	10	2.52	2.42	
10	10	2.50	2.40	
		Average	2.46	
10	10	.92	.82	Same as above, filtered.
10	10	1.03	.93	
10	10	1.00	.90	
10	10	.95	.85	
10	10	1.00	.90	
		Average	1.88	

* Correction for distilled water 0.1 parts per million.

determination of iron when hydrochloric acid is present. He claims that the action of hydrochloric acid upon the permanganate may be prevented by the addition of mercuric sulphate. Mercuric sulphate is highly ionized and so also is the hydrochloric acid. Mercuric chloride, however, is only slightly ionized. Thus when the mercuric sulphate is added to hydrochloric acid the slightly ionized mercuric chloride is formed, and the chlorine ions are removed from the solution.

The action of chlorides in the oxygen consumed test is analagous and it was thought that it might be possible to make use of the mercuric sulphate in this test when the chlorides were present.

The solutions used were the regular solutions with sodium oxalate substituted in place of the oxalic acid, and mercuric sulphate was added.

STANDARD SODIUM OXALATE. Owing to the fact that $Na_2C_2O_4$ does not contain water of crystallization and is not hygroscopic it was considered to be better for standardization purposes, than either the ammonium oxalate or oxalic acid.

MERCURIC SULPHATE SOLUTION. This was prepared as described by Cady with the exception that no phosporic acid was used. Two hundred g. of the mercuric sulphate, free from the mercurous salt, were mixed with 80 c.c. of concentrated H_2SO_4 and this pasty mass was diluted carefully to one liter. This solution if carefully prepared will contain no yellow basic salt. If this salt forms, more sulphuric acid will cause it to go into solution.

I. Five determinations were first made on distilled water following the usual method.

II. Then five determinations were made on distilled water to which sodium chloride had been added in such amounts that the

water contained 100 parts per million of chlorine.

III. Five determinations were made on the above water containing the chlorides, and after being acidified with concentrated H_2SO_4 10 c.c. of the $HgSO_4$ solution were added. Then the determinations were carried out as usual. The manipulation was as follows:

10 c.c. of the sample of water were placed in an Erlenmeyer flask, 2 c.c. of concentrated c. p. H_2SO_4 added, (and when $HgSO_4$ is used 10 c.c. of that solution are added at this point), 10 c.c. of standard $KMnO_4$ solution added, placed in boiling water bath for exactly 30 minutes, 10 c.c. of standard $Na_2C_2O_4$ solution added and the excess titrated with standard $KMnO_4$. The results of four series of determinations are given in the table of data, Series IV.

Sub-Series No. I. shows that 100 c.c. of distilled water required 0.1 c.c. of $KMnO_4$ to give a distinct pink color.

Sub-Series No. II. shows that the presence of 100 parts per million of chlorides makes a decided difference,(0.18 parts per million) in the amount of oxygen consumed.

Sub-Series No. III. shows, first, that the addition of $HgSO_4$ causes the results for oxygen consumed to come high. Second, it gives results which do not check closely with each other. This is doubtless explained by the fact that the end point obtained when $HgSO_4$ is used is very unreliable. A pink color appears but immediately begins to fade, and a much larger amount of $KMnO_4$ is used before a permanent pink is obtained. This gives results for oxygen consumed which are much too high.

Sub-Series IV. A fourth sub-series of five determinations was carried out. The numerical results of which are given in the table of data (Sub-Series IV.). In this series the $HgSO_4$ which was used was previously treated with $KMnO_4$ until a slight pink color was

imparted to the solution. This was done with the thought that if $KMnO_4$ was added to the $HgSO_4$ until a pink color was obtained, in the final titration with $KMnO_4$ the results would be normal. The end point in this series was not sharp, but acted much the same as in the case preceeding. The values which were obtained for the "Oxygen Consumed" were from three to four times as large as those obtained when $HgSO_4$ was not used, (see Sub-Series No. II). Our experiments show no advantage in the use of the sulphate of mercury.

SERIES IV.

Sub-Series	c.c. of Water	c.c. of H_2SO_4	c.c. of $HgSO_4$	c.c. of $KMnO_4$	c.c. of $Na_2C_2O_4$	c.c. of $KMNO_4$	Parts per Million
I	100	2	0	10	10	0.10	0.10
	100	2	0	10	10	0.15	0.15
	100	2	0	10	10	0.10	0.10
	100	2	0	10	10	0.10	0.10
	100	2	0	10	10	0.10	0.10
	Distilled water containing 100 parts per million of chlorides.						
II.	100	2	0	10	10	1.82	1.72?
	100	2	0	10	10	.33	.23
	100	2	0	10	10	.25	.15
	100	2	0	10	10	.20	.10
	100	2	0	10	10	.35	.25
	Same as No. II. using $HgSO_4$.						
III.	100	2	10	10	10	1.30	1.20
	100	2	10	10	10	.95	.85
	100	2	10	10	10	1.10	1.00
	100	2	10	10	10	.87	.77
	100	2	10	10	10	.98	.88
	Same as No. II. using $HgSO_4$ pink by permanganate*						
IV.	100	2	10	10	10	.90	.80
	100	2	10	10	10	.75	.65
	100	2	10	10	10	1.00	.90
	100	2	10	10	10	.90	.80
	100	2	10	10	10	.80	.70

*Enough $KMnO_4$ was added to $HgSO_4$ used to just give it a pink tint.

PART II.

DETERMINATION OF NITRATES.

The two most important methods now used in the determination of nitrates in water are the Phenol Sulphonic Acid Method, and the Aluminium Reduction Method. Other methods have been proposed from time to time but not generally adopted. A recent colorometric method in which brucine is used is recommended.

The Phenol Sulphonic Acid method depends upon the fact that when a sample of water is evaporated to dryness and the residue is treated with phenol-sulphonic acid, diluted and made alkaline with ammonia, a greenish yellow color is produced, due to the formation of ammonium nitro-phenols, which is proportional to the amount of nitrate present. By comparison with standards the amount of nitrogen present as nitrate can be determined.

In the Aluminium method the nitrate in the water is reduced to ammonia by the action of mascent hydrogen, which is generated by the action of aluminium and sodium hydroxide, or potassium hydroxide on the water. $Al + H_2O + NaOH = NaAlO_2 + 3H$. The ammonia thus formed is determined directly by nesslerization or the solution is distilled and the distillate nesslerized.

The Brucine method depends upon the fact that when a solution of brucine in sulphuric acid is added to a water containing a nitrate, an orange or rose color is produced.

Of the three methods the phenol sulphonic acid method is the most used, while the aluminium reduction method holds the second place. There are serious objections to all three methods. The

presence of chlorides interferes with the phenol sulphonic acid method. They may be precipitated out by silver sulphate, but this is not very practical. The aluminium method is said to give low results*, requires somewhat more time, but is not affected by the presence of chlorides. The Brucine method is rather expensive and the results can not always be relied upon.

A comparison of the results obtained by the three methods was made. The manipulation of the three methods was as follows:

The Phenol Sulphonic Acid Method, from Standard Methods of Analysis, American Public Health Association. Ten c.c. or more of the sample to be treated is evaporated to dryness on the steam bath, and 2 c.c. phenol sulphonic acid are added and the two are mixed, diluted with a little distilled water and made alkaline with ammonium hydroxide, washed into Nessler tubes and diluted to 50 c.c. These are allowed to stand for a short time and are then compared with standards prepared in a similar way, using known amounts of a standard solution of potassium nitrate.

The Aluminium Reduction Method. One-hundred c.c. of the sample of water are measured into a porcelain casserole and 2 c.c. of a concentrated solution (nitrate free) of NaOH* or KOH are added. This mixture is placed on a Bunsen burner and evaporated to about 20 c.c., poured into a large wide mouthed test tube and diluted to about 75 c.c. with (NH_3 free) water. When the solution has come to room temperature a strip of aluminium** is added and the reduction is allowed to continue over night at room temperature. The solution is then washed into a Kjeldahl flask and distilled. (The distilling

---

* Chem. News, Vol. 62, 1890.

* 300 g. per liter nitrate free by reduction with Al.

** Aluminium strips 1/4" X 4". Weight about 0.5 gr.

apparatus must be steamed out before this distillation to insure the absence of ammonia). The distillate is caught in 200 c.c. flasks, 50 c.c. (or when necessary a smaller amount) of the distillate are nesslerized.

Brucine Method, by Noll*. To 10 c.c. of water to be tested is added 20 c.c. of a solution of brucine in sulphuric acid (.05 g. in 20 c.c. of acid 1.84) solution made up when used. This solution is allowed to act upon the water for just 15 seconds, then the mixture is poured into a Hehner cylinder containing 70 c.c. of distilled water. By drawing out the solution from this cylinder or from the similar cylinder containing a standard amount of nitrate until the colors are identical, the amount of nitrate present is determined from the amount of nitrate in the standard cylinder which matches in color the unknown solution in the other cylinder.

Ten waters were chosen from the laboratory samples. Care was taken to have representative samples containing widely varying amounts of nitrogen as nitrate. These were analyzed by the three methods and the results are shown in Table I . It will be noticed that by the Aluminium Reduction method the different analyses of the same water did not check. This is perhaps due to the fact that from 3 to 5 days elapsed between the different sets of analyses.

From this table it is evident that the three methods do not check each other. Since the action of the bacteria in a natural water keeps the nitrate content constantly changing, it was thought best to prepare a series of waters containing known amounts of nitrates. Such a series was prepared and analyzed by the three methods.

---

*Abs. Jour. Chem. Soc. 1902, 173.

*Zeit. Angew. Chem. 1901, 14, 1317.

TABLE I.

DETERMINATION OF NITRATES IN SERIES OF TEN WATERS BY DIFFERENT METHODS.

Serial Number	Aluminium Reduction Method.			Phenol Sulphonic Acid Method.	Brucine, Sulphuric Acid Method.	
16924	0.000	0.280	5.200	0.050	0.130	0.100
16922	0.080	0.080	0.360	0.025	0.090	0.090
16948	0.360	0.360	0.440	0.215	0.150	0.190
16938	0.800	0.680	1.160	1.630	2.550	2.000
16921	2.000	3.600	10.400	8.000	6.710	6.570
16914	3.970	2.800	6.600	7.520	7.400	5.640
16926	8.000	16.000	36.000	32.000	11.100	14.080
16955	22.400	16.000	45.000	15.400	9.800	13.600
16944	35.000	20.000	60.000	70.200	11.700	15.700
16912	72.000	38.000	120.000	120.000	11.200	19.000

The Results are shown in Table II. Here it will be seen there is no regular increase or decrease in the amounts of nitrates found. But, as before, it also shows that the three methods did not check, and did not give results which correspond to the amount of nitrate present. It will be noted also that the aluminium method gave for small amounts high results and for the larger amounts low results, while the phenol sulphonic acid method gave high results in all cases.

In the case of the brucine method there was no regularity. We obtained both low and high results, which are, as a rule, quite close to the theoretical.

STUDY OF THE BRUCINE METHOD. A series of waters of known nitrate content was analyzed. The results did not check well with the theoretical. A possible explanation of bad results lay in difficulty of correctly matching the colors of the unknown with those in the standard tubes. A small error here would mean a large error in the final result. This suggested the use of "Nessler" tubes and a study of the (1) effect of dilution.

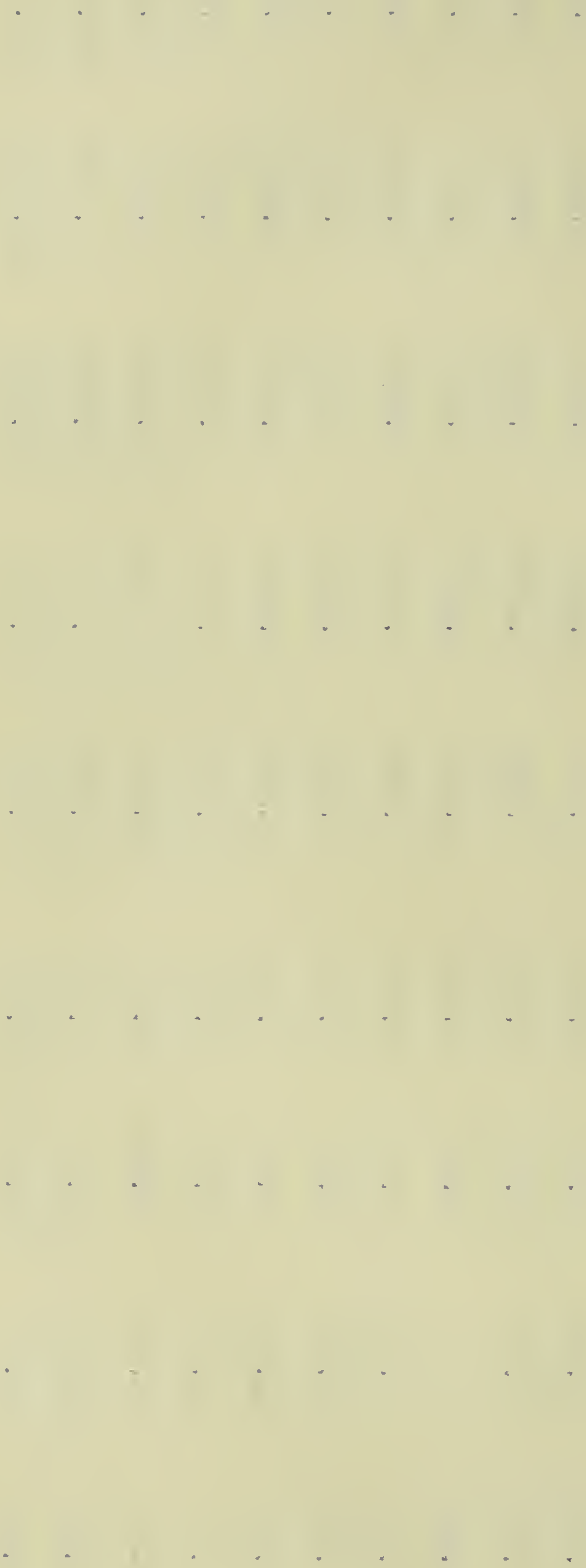
The method of Noll states that the time of action of the Brucine solution upon the water before dilution must be just 15 seconds in order to get good results. If this be the case a difference of a few seconds in the time of action must make a great difference in the results. For such a small period of time errors which are comparatively large are inevitable. If a (2) longer period of time could be used the relatively large error would be eliminated.

The solution of Brucine Sulphuric Acid, according to Noll, must be made up on the same day in which it is to be used. This required considerable time and the question came up, (3) what would be the effect of using an older solution?

TABLE II.

DETERMINATION OF NITRATES IN A SERIES OF TEN WATERS OF KNOWN NITRATE CONTENT.

Amount of Nitrates present in Series of Waters.	Aluminium Reduction Method.			Phenol Sulphonic Acid Method		Brucine Sulphuric Acid Method.		
0.05	0.36	0.20	0.12	0.10	0.075	0.117	0.140	0.052
0.10	0.20	0.20	0.24	0.025	0.150	0.115	0.160	0.066
0.25	----	0.40	0.28	0.325	0.310	0.232	0.250	0.170
0.50	0.60	0.52	0.40	0.685	0.575	0.670	0.130	0.350
1.00	0.92	0.92	0.60	1.130	1.250	1.080	1.400	0.500
2.50	2.00	2.24	1.80	3.300	3.240	3.600	2.600	2.600
5.00	4.48	4.00	3.36	11.500	3.500	5.700	3.250	3.500
10.00	8.60	8.48	7.04	13.000	10.000	11.200	7.500	6.700
25.00	20.80	20.80	17.20	30.000	21.000	23.750	16.250	19.000
50.00	34.00	50.00	33.00	60.000	50.000	45.500	33.000	37.000



I. Does the color produced in solutions containing different amounts of nitrates differ proportionally when examined in Nessler tubes? Three samples of water containing respectively 2, 5 and 10 c.c. of a standard nitrate solution were diluted to a volume of 10 c.c. Then they were treated with brucine sulphuric acid according to the method of Noll. The first volume in each case was 100 c.c. These were placed in flasks and numbered respectively 1, 2, 3. From flask No. I (the one containing 2 c.c. of the standard nitrate) 5 c.c. were removed and placed in a Nessler tube. From flask No. 2 (the one containing 5 c.c. of the standard nitrate) 2 c.c. were removed, and from flask No. 3, 1 c.c. The solutions in the three Nessler tubes were diluted to 50 c.c. and compared. The colors obtained were of different tints and of different strengths. By uniform treatment like the above the colors should be identical. This shows that the color produced is not proportional to the amount of nitrate present.

II. What will be the effect of a longer action of the brucine sulphuric acid solution upon the water before dilution? Three samples of water with varying nitrate content were analyzed by the method of Noll in which the time of action is fifteen seconds. At the same time the three samples were analyzed and the period of time that the brucine sulphuric acid was allowed to act was changed from fifteen seconds to five minutes. It was found that when the period of action was increased from 15 seconds to 5 minutes the color produced was in each case decidedly less.

III. What is the effect of using a brucine sulphuric acid solution which has been prepared more than twenty-four hours? A series of experiments were made in which the colors produced by

an old brucine sulphuric acid solution were compared with those produced by a freshly prepared solution. The brucine sulphuric acid solution upon standing some time becomes brown in color. It was found that the older solution gave a deeper color than the freshly prepared solution.

The Use of Brucine and Oxalic Acid, by J. West Knights* The method consisted in evaporating 10 c,c, of the sample of water to dryness on the steam bath, treating the residue with from .5 c.c. to 3. c.c. of brucine solution (1 g. brucine in 100 c.c. of alcohol) and adding six drops of a saturated solution of oxalic acid, evaporating to dryness, taking up with water, evaporating to dryness again, and diluting to 100 c.c. The color produced must be red, not brown or pink. When carbonates or calcium salts were present filtration was found necessary before reading.

A water containing a known amount of nitrate was analyzed by the above method. A good color was produced. Portions of the solution were measured into Nessler tubes and diluted to 50 c.c. These were used as standards.

A series of waters containing amounts of nitrates varying from .05 to 50. parts per million were analyzed, and the colors obtained compared with the standards. The comparison showed no relation between the amount of nitrate and the color.

The question arose as to the possibility of substituting some other acid in place of the oxalic acid and thus avoiding the precipitation of oxalates. Succinic and malonic acid were tried but no color was produced. Hydrochloric acid was used and this gave a color, but the tint varied greatly with the different amounts of

---

*Analyst, Vol. VII. 1881, 56.

nitrates. A series of waters was analyzed using dilute H_2SO_4 in place of the oxalic acid. The solution would not evaporate to dryness on the steam bath after the addition of the sulphuric acid. After the evaporation of the alcohol from the brucine solution, the addition of water produced, when large amounts of nitrate were present, a deep cherry red color. As the amount of nitrate decreased, the color produced changed, first, to a yellowish red, and then to a faint pink. The colors produced at first seemed to be proportional to the nitrate present, but upon careful examination it was found that the colors were not proportional. The colors deepened a little upon standing. It was noticed that the water which contained only .05 parts per million of nitrates gave a distinct color. This shows the delicacy of the test in a qualitative way. From these tests we do not feel ready to recommend the adoption of the method.

SPECIAL INVESTIGATION OF THE ALUMINIUM REDUCTION METHOD.

Historical-: Schulze* in 1861 made the discovery that nitric acid or nitrates could be reduced to ammonia by nascent hydrogen generated by the action of zinc, sodium amalgam or aluminium in a strongly alkaline solution. In 1869 he published a method* for the determination of nitrates. In this method he used aluminium in a sodium hydroxide solution to reduce the nitrates to ammonia.

A few years later the zinc copper couple was used for the reduction. In 1888, Ormandy & Cohn* recommended the use of mercury aluminium couple. They claimed that by the use of this couple the reduction could be completed in one hour while with the zinc copper couple the reduction required at least six hours.

Hazen and Clark* investigated the distillation of the ammonia to determine the percent of ammonia lost and the cause of this loss. They found only about 90 percent of the ammonia which was present before distillation. They state, after making experiments, that there is no loss from incomplete condensation, but that the low

---

* Central Blatt, 42, p. 186

*Zeit. fur. Anal. Chem. Vol. 2, p 311.

*Jour. Chem. Soc. Vol. 57, p. 811.

*Chem. News. 1890, Vol. 62

results are due to the fact that the distillate is at a lower temperature than the standard solution, when nesslerized. And that this difference in temperature causes a difference in the color produced by the Nessler solution.

In a later article by Hazen and Clark* there is given a description of the aluminium process as described in Sutton's "Volumetric Analysis". A 40 per cent sodium hydroxide solution was used to expel the ammonia present and when the solution had cooled aluminium foil was added. The hydrogen which was evolved was passed through dilute acid to hold any ammonia it might carry. The acid was added to the water after the reduction was completed.

They make the further statements that the amount of ammonia carried away by the hydrogen is so small that it is better to calculate it than to try to determine it. They estimate a loss of 3.5 per cent and their experiments show a loss of about 2. per cent. They also state that on ground waters, direct nesslerization without distillation is successful.

They continue their work with an investigation of the amount of aluminium and the strength of the sodium hydroxide solution required for the best results.

Woy* uses an alloy of aluminium, copper and zinc in sodium hydroxide solution for the reduction. He distills the reduced solution into standard acid and titrates.

---

*Chem. News. Vol. 64, 1891, p. 162.

---

*Zeit. öffentl. Chem. 1902, 8, 301.
*
Jour. Chem. Soc. (abs) 1902 ii 694.

Experimental-: A series of determinations, (Table III a and b) were made according to the regular proceedure of the aluminium method. Distilled water containing ten parts per million of N as nitrates was used. In these we attempted to ascertain the percentage of nitrogen as nitrate that could be recovered under various conditions of temperature and time of reduction, and we studied the possibility of direct nesslerization. From an inspection of Table III the following conclusions were drawn:

1. At room temperature, with 16 hours reduction, there was recovered about 72.3 per cent of the N as nitrate present. At a temperature of 37.5° C. with 16 hours reduction, there was recovered about 35 per cent of the N. as nitrate present. At the temperature of the icebox (5° - 8° C.) with 16 hours reduction, there was recovered about 86 per cent of the nitrates present.

The amount of nitrate recovered varies with the temperature, being greatest at the temperature of the ice box, and least at a temperature of 37.5° C. The amount of nitrate recovered after a reduction period of 32 hours at each of the three temperatures was less than that recovered after 16 hours reduction.

The results obtained by direct nesslerization check well with those obtained by distillation before nesslerization, and indicate that in certain waters direct nesslerization can be successfully used.

This Table (III) would indicate that with the usual manipulation a large percentage of the nitrates present are lost. This conclusion is confirmed by a later experiment (see Table IX.)

It has been already determined by some investigators* that

---

* Chem. News. Vol.64, 162.

TABLE III. (a).

Room temperature, 16 hours, water containing ten parts per million nitrates.

I.	c.c. of Water	Vol. of Distillate	Volume used	c.c. of Standard	Parts per Million.
Blank	100	200	50	0.6	0.24
1	100	200	10	3.5	7.00
2	100	200	10	3.8	7.60
3	100	200	10	3.5	7.00
4*	100	200	10	3.7	7.40
II. For 16 hours at a temperature of from 35°-40°C.					
Blank	100	200	50	1.0	.40
1	100	200	25	4.5	3.60
2	100	200	25	4.5	3.60
3	100	200	25	3.8	3.00
4*	100	200	25	4.2	3.40
III. For 16 hours at temperature of ice-box from 5°-8° C.					
Blank	100	200	50	1.2	.48
1	100	200	10	4.3	8.60
2	100	200	10	4.3	8.60
3	100	200	10	4.2	8.40
4*	100	200	10	4.3	8.60

*Indicates that after reduction solutions diluted to 200 c.c. and nesslerized directly. All others were distilled before nesslerization.

TABLE III. (b).

Room temperature, 32 hours, water containing 10 parts per million nitrates.

I.	c.c. of Water	Vol. of Distillate	Volume used	c.c. of Standard	Parts per Million.
Blank	100	200	50	1.1	.44
1	100	200	10	2.7	5.40
2	100	200	10	3.0	6.00
3	100	200	10	2.5	5.00
4*	100	200	10	2.7	5.40
II. For Thirty-two hours at a temperature of from 35°-40° C.					
Blank	100	200	50	.6	.24
1	100	200	25	3.2	2.56
2	100	200	25	3.3	2.64
3	100	200	25	3.1	2.48
4*	100	200	25	3.0	2.40
III. For thirty-two hours at temperature of the ice box from 5°-8° C.					
Blank	100	200	50	1.0	.40
1	100	200	10	4.0	8.00
2	100	200	10	3.8	7.60
3	100	200	10	4.0	8.00
4*	100	200	10	4.2	8.40

* Indicates that after reduction solutions diluted to 200 c.c. and nesslerized directly. All others were distilled before nesslerization.

the hydrogen passing off from a solution during reduction does not carry much ammonia with it. In determining the ammonia thus carried away with the hydrogen, it is necessary to stopper the tube in which the reduction takes place and pass the hydrogen gas through an absorbent solution such as dilute hydrochloric acid, which will absorb the ammonia.

In order to show the amount and rate of the loss of ammonia the series of determinations shown in Table IV were made on distilled water to which ten parts per million of N as nitrates had been added. The reduction tubes were stoppered with one hole rubber corks, bearing a delivery tube which dipped into dilute hydrochloric acid in small test tubes. These tubes were replaced every hour for a period of six hours, and diluted in nessler tubes to 50 c.c., and the amount of ammonia determined by nesslerization. The reduction was then continued 14 hours with one set of trap tubes, which were then diluted to 50 c.c. and nesslerized. This gave the amount of ammonia lost during 20 hours reduction when traps were used. The solutions in the reduction tubes were diluted to 200 c.c. with ammonia free water and aliquot portions were nesslerized directly and the ammonia determined.

As shown by Table IV the amount of ammonia caught in the traps is very small. The higher the temperature at which the determination is made the larger the amount of ammonia found in the traps. The ammonia found in the reduction tubes after 20 hours showed that all of the nitrate had been reduced and that the loss was practically zero. By comparing the percent of nitrate found here with that found in Table III when traps were not used, it is evident that by use of traps better results are obtained. This lead

Ammonia found
duction tube

Number	c.c. of Water	Volume of Dilution	Volume used
1	100	200	5
2	100	200	5
3	100	200	5
4	100	200	5
1	100	200	5
2	100	200	5
3	100	200	5
4	100	200	5
1	100	200	
2	100	200	
3	100	200	
4	100	200	

*Trap tubes we

**Trap tubes c

TABLE IV.

LOSS OF AMMONIA DURING REDUCTION WITH TRAPS.

Direct nesslerization, total period of time 20 hours, ten parts per million nitrate present.

Ammonia found in reduction tubes.						Ammonia in traps during six hours reduction*															
						1st. hour		2nd hour		3rd hour		4th hour		5th hour		6th hour					
Number	c.c. of Water	Volume of Dilution	Volume used	c.c. of Standard	Parts per Million.	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million.	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million.	Total NH_3 in Traps.	Total NH_3 found.	c.c. of Standard**	Parts per Million**
									I. Room temperature.												
1	100	200	5	2.5	10.0	0.0	.00	.2	.02	.1	.01	.0	.00	.1	.01	.1	.01	.10	10.10	.5	.05
2	100	200	5	2.3	9.2	.0	.00	.2	.02	.0	.00	.0	.00	.1	.01	.4	.04	.11	9.31	.4	.04
3	100	200	5	2.6	10.4	.0	.00	.1	.01	.2	.02	.0	.00	.1	.01	.0	.00	.05	10.45	.1	.01
4	100	200	5	2.4	9.6	.0	.00	.3	.03	.1	.01	.0	.00	.1	.01	.1	.01	.10	9.70	.4	.04
									II. Temperature 37 1/2°C.												
1	100	200	5	2.5	10.0	.0	.00	.2	.02	.4	.04	.1	.01	.2	.02	.1	.01	.18	10.18	.8	.08
2	100	200	5	2.5	10.0	.9	.09	.3	.03	.4	.04	.1	.01	.2	.02	.1	.01	.29	10.29	.9	.09
3	100	200	5	2.4	9.6	.2	.02	.0	.00	.3	.05	.1	.01	.1	.01	.2	.02	.17	9.77	.8	.08
4	100	200	5	2.6	10.4	.3	.03	.6	.06	.3	.03	.1	.01	.1	.01	.1	.01	.23	10.63	.8	.08
									III. Ice-box temperature (5 -10°C.)												
1	100	200	5	2.5	10.0	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.00	10.00	.0	.00
2	100	200	5	2.0	8.0	.0	.00	.0	.00	.1	.01	.0	.00	.0	.00	.0	.00	.01	8.01	.0	.00
3	100	200	5	2.4	9.6	.0	.00	.1	.01	.0	.00	.0	.00	.0	.00	.0	.00	.02	9.62	.1	.01
4	100	200	5	2.5	10.0	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.0	.00	.01	10.01	.1	.01

*Trap tubes were removed at the end of each hour for a period of six hours and nesslerized.

** Trap tubes containing NH_3 for the last 14 hours of the 20 hours reduction.

to a series of determinations part of which were made using the traps, while the others were run without traps. (Table V.)

The reduction was continued for ten hours. The water used contained ten parts per million of N as nitrates, as in the previous series. The ammonia found in the traps was very low. The ammonia found in the reduction tubes in which traps had been used indicated that there had been no loss. In the case when traps were not used the results are uniformly low. It seems peculiar that, when there is such a loss of ammonia during reduction without using the traps, it is impossible to recover this amount of ammonia when traps are used. We could account for this by the fact that the trap creates a slight pressure within the reduction tube and prevents rapid diffusion of the light gases, hydrogen and ammonia. The larger per cent of the gas confined in the reduction tube will be hydrogen, which will pass off through the trap quite slowly, allowing all or nearly all of the ammonia carried from the solution by the hydrogen to be redissolved.

The results shown in Tables IV and V also confirm the results shown in Table III, that the best results are obtained at the lowest temperature. This indicates that with the more rapid evolution of the hydrogen more of the ammonia is carried away. In the determination without the traps, at the temperature of the ice box about 80 per cent of the nitrates present were recovered. At room temperature about 60 per cent and at 37.5 ° C. about 46 per cent. The reduction in the open tubes when continued for a long period of time gave a decrease in the amount of nitrate found. This would indicate that the reduction was already complete and that the ammonia was being lost, undoubtedly being carried away by the hydrogen.

TABLE V.

(With Traps) COMPARISON WITH AND WITHOUT TRAPS.-- 10 HOURS. (Without Traps)

				Room Temperature						
I.	c.c. of Water	Vol. of Dilution	Volume used	c.c. of Standard	Pts.per Million	c.c. of Water	Vol. of Dilution	Volume used	c.c. of Standard	Pts. per Million
1.	100	200	5	2.5	10.0	100	200	5	1.4	5.6
2.	100	200	5	2.3	9.2	100	200	5	1.6	6.4
3.	100	200	5	2.5	10.0	100	200	5	1.5	6.0
4.	100	200	5	2.5	10.0	100	200	5	1.5	6.0
II.	Temperature 37 1/2°C.									
1	100	200	5	2.5	10.0	100	200	5	1.2	4.8
2	100	200	5	2.5	10.0	100	200	5	1.1	4.4
3	100	200	5	2.5	10.0	100	200	5	1.1	4.4
4	100	200	5	2.5	10.0	100	200	5	1.2	4.8
III.	Temperature of ice box. (5°-8°C)									
1	100	200	5	2.5	10.0	100	200	5	2.0	8.0
2	100	200	5	2.5	10.0	100	200	5	2.0	8.0
3	100	200	5	2.5	10.0	100	200	5	2.1	8.4
4	100	200	5	2.5	10.0	100	200	5	2.1	8.4
	Ammonia found in traps.									
1.	100			1.0	.10	I. Room Temperature.				
2	100			0.8	.08					
3	100		(Cloudy)	---	----					
4	100			0.9	.09					
1	100			1.3	.13	II. Temperature 37 1/2°C.				
2	100			1.6	.16					
3	100			1.5	.15					
4	100		(Cloudy)	---	----					
1	100			0.8	.08	III. Temperature Ice-Box (5°-8°)				
2	100			0.8	.08					
3	100			0.4	.04					
4	100			0.6	.06					

One of the objections to the aluminium method lies in the fact that a long period of time is required for complete reduction. A series of determinations was undertaken to ascertain the time required for complete reduction. Twenty tests were made. Traps were used. The reducing action was stopped and the amount of ammonia determined in four tests every two hours. The results of these experiments are shown in Table VI. It was shown that in distilled water to which ten parts per million of N as nitrates had been added the reduction at room temperature is complete in less than four hours.

A similar series of sixteen determinations was made at 37.5° C. to ascertain if at the highest temperature the reduction was completed in a shorter period of time. Four from this series were removed and the amount of ammonia determined every hour for four hours. The results of this series as found in Table VII show that, in distilled water containing ten parts per million of nitrogen as nitrates, the reduction at 37.5° C. is complete in less than three hours. We regret that we have no data to show whether reduction is complete at the end of three hours at room temperature.

A series of determinations (Table VIII) was made on two samples of distilled water, containing 0.5 parts and 2.5 parts per million of nitrates, respectively. The results obtained were uniform and close to the theoretical.

Three blank determinations were made upon distilled water.

Two determinations were made on water from Lake Michigan which is low in nitrates. The results showed .42 parts per million.

Table IX (a) shows the results of analyses of six Survey waters using traps and allowing the reduction to continue four hours. Compared with the results obtained by the regular laboratory proceedure the results obtained by the regular method are all low, in-

TABLE VI.

TIME REQUIRED FOR COMPLETE REDUCTION.

Direct nesslerization, using traps, Room temperature, ten parts per million.

Time of Treatment	No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	NH$_3$ in Traps.	
							c.c. of Standard	Parts per Million.
I.*	1	100	200	5	1.9	7.6	0.3	.03
Two Hours	2	100	200	5	1.9	7.6	0.2	.02
	3	100	200	5	2.0	8.0	0.2	.02
	4	100	200	5	1.9	7.6	0.2	.02
II.	1	100	200	5	2.5	10.0	0.6	.06
Four Hours	2	100	200	5	2.5	10.0	0.5	.05
	3	100	200	5	2.6	10.4	0.6	.06
	4	100	200	5	2.5	10.0	0.6	.06
III.	1	100	200	5	2.6	10.4	0.8	.08
Six Hours	2	100	200	5	2.6	10.4	0.7	.07
	3	100	200	5	2.6	10.4	0.8	.08
	4	100	200	5	2.8	11.0	0.7	.07
IV.	1	100	200	5	2.6	10.4	0.9	.09
Eight Hours	2	100	200	5	2.5	10.0	0.9	.09
	3	100	200	5	2.5	10.0	0.9	.09
	4	100	200	5	2.5	10.0	0.7	.07
V.	1	100	200	5	---	----	---	---
Ten Hours	2	100	200	5	2.6	10.4	0.8	.08
	3	100	200	5	2.5	10.0	1.2	.12
	4	100	200	5	2.7	10.8	1.0	.10

*Nitrites were found to be present approximately 0.02 parts per million.

TABLE VII.

TIME REQUIRED FOR COMPLETE REDUCTION.

Direct nesslerization, using traps, temperature 37 1/2°C., ten parts per million.

Time of Treatment	No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	NH_3 in Traps. c.c. of Standard	NH_3 in Traps. Parts per Million
I. One Hour	1	100	200	5	.9	3.6	.3	.03
	2	100	200	5	1.2	4.8	.0	.00
	3	100	200	5	1.4	5.6	.0	.00
	4	100	200	5	1.1	4.4	.2	.02
II. Two Hours.	1	100	200	5	2.3	9.2	.4	.04
	2	100	200	5	2.1	8.4	.2	.02
	3	100	200	5	2.2	8.8	.3	.03
	4	100	200	5	2.3	9.2	.3	.03
III. Three Hours	1	100	200	5	2.5	10.0	.4	.04
	2	100	200	5	2.6	10.4	.3	.03
	3	100	200	5	2.6	10.4	.1	.01
	4	100	200	5	2.6	10.4	.5	.05
IV. Four Hours	1	100	200	5	2.7	10.8	.4	.04
	2	100	200	5	2.8	11.2	.5	.05
	3	100	200	5	2.7	10.8	(Cloudy)	
	4	100	200	5	2.7	10.8	.4	.04

TABLE VIII.

TREATMENT OF DISTILLED WATERS CONTAINING .5 and 2.5 PARTS PER MILLION.NITRATES. *

No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	NH_3 in Traps.	
						c.c. of Standard	Parts per Million
I. Five tenths of a part per million of nitrates.							
1	100	200	50	1.3	0.52	.3	.03
2	100	200	50	1.3	0.52	.3	.03
3	100	200	50	1.4	0.56	.3	.03
4	100	200	50	1.3	0.52	.4	.04
II. Two and five tenths parts per million of nitrates.							
1	100	200	10	1.3	2.6	.4	.04
2	100	200	10	1.35	2.70	.8	.08
3	100	200	10	1.2	2.4	.4	.04
4	100	200	10	1.2	2.4	.5	.05
III. Blank on Distilled water.							
1	100	200	50	0.4	.16	.2	.02
2	100	200	50	0.4	.16	.0	.00
3	100	200	50	0.8	.32	.0	.00
IV. Water from Lake Michigan.							
1	100	200	50	1.1	.44	.0	.00
2	100	200	50	1.0	.40	.0	.00

*Direct nesslerization, room temperature, four hours reduction, using traps.

TABLE IX. (a)

ANALYSIS OF SIX SURVEY WATERS.

Direct nesslerization, room temperature, four hours reduction, using traps, compared with regular laboratory method.

Direct nesslerization, room temperature, four hours reduction, using traps.						NH_3 in Traps.		Results using regular laboratory method
No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Mill.	Parts per Mill.
17606	100	200	50	1.1	0.44	.0	.00	0.12
17607	100	200	1	2.1	42.00	.8	.08	30.00
17608	100	200	50	1.1	0.44	.0	.00	0.32
17609	100	200	1	1.5	30.00	.6	.06	25.00
17610	100	200	5	1.7	6.8	.0	.00	4.24
17611	100	200	5	0.8	3.2	.0	.00	1.59

TABLE IX. (b)

ANALYSIS OF SERIES OF WATERS OF KNOWN VARYING NITRATE CONTENT.

Direct nesslerization, room temperature, four hours reduction, using traps.

						NH_3 in Traps		Known amounts of nitrates present.
No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Mill.	Parts per Mill.
I 1	100	200	50	0.5	0.20	.0	.00	.05
2	100	200	50	0.5	0.20	.4	.04	.05
II 1	100	200	50	1.1	0.44	.00	.00	.10
2	100	200	50	1.0	0.40	.1	.01	.10
III 1	100	200	10	0.6	1.20	.0	.00	1.00
2	100	200	--	---	---	--	---	1.00
IV 1	100	200	5	1.3	5.2	.1	.01	5.0
2	100	200	5	1.3	5.2	.5	.05	5.0
V 1	100	200	1	1.3	26.0	.7	.07	25.0
2	100	200	1	1.3	26.0	.8	.08	25.0

dicating again that there is some loss during reduction.

Table IX (b) shows the results from the analysis of five waters, run in duplicates, containing varying amounts of nitrates. The results are all high indicating the probability of N as nitrate in the reagents or distilled water.

Table X shows the results of a series of determinations made on five samples of distilled water to which varying amounts of nitrates had been added. The amount of nitrate added was not known to the analyst. Two blanks were made using distilled water and the sodium hydroxide which had been used for the previous determinations. One blank was run using specially prepared potassium hydroxide and all glass connections. In the determinations thus far made we have not been able to obtain a perfect blank. The determinations made give us an average blank of about 0.16 parts per million.

Determination of nitrates in Polluted Streams and Sewages- Having found by experiment that N as nitrates added in distilled water could be recovered, and N as nitrate in drinking waters could be quite successfully determined, by four hours reduction, using traps, it was thought advisable to study the possibility of using this method of prodeedure for waters from polluted streams and for sewages.

It is well known that nitrates in sewages are very low, seldom, if ever, exceeding 0.3 parts per million and more often only a few hundredths parts per million. Several series of analyses were made upon three types of polluted waters, e. g. a polluted stream and the inflow and outflow of the Urbana Septic Tank. Since each of these three types of waters was low in nitrates, it was

TABLE X.

TREATMENT OF SERIES OF DISTILLED WATERS CONTAINING VARYING AMOUNTS OF NITRATES.*

Direct nesslerization, room temperature, four hours reduction, using traps.

No. *	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	NH_3 in Traps. c.c. of Standard	NH_3 in Traps. Parts per Million.
I.	100	200	1	1.2	24.0	.0	.0
II.	100	200	5	2.5	10.0	.0	.0
III.	100	200	10	1.0	2.0	..0	.0
IV.	100	200	50	0.4	0.16	.0	.0
V.	100	200	50	1.0	.40	.0	.0
Blanks on distilled water with the NaOH ordinarily used.							
I.	100	200	50	0.2	.08	.0	.0
II.	100	200	50	0.6	.24	.0	.0
Blank with specially prepared KOH and glass connections.							
I.	100	200	50	0.3	.12	.3	.03

* The amounts in the series I - V were respectively 22.0, 10.8, 2.8, 0.0, and 0.28, and were unknown to the analyst at the time of analysis.

thought best in order to determine the efficiency of the method, to add a known amount of nitrates to each of the samples, and then make determinations on the original waters and also on those to which the nitrate had been added. A series of determinations was made and the results are shown in Table XI. The results of a similar series of determinations made on samples of the same waters collected a few days later are shown in Table XII.

In both of these series the nitrate was added 24 hours before the determinations were started. This gave the bacteria present in the water considerable time to act upon the nitrates added. Tables Xi and XII show that in no case is the amount of nitrate found equal to the sum of the nitrate already present and that added. This indicates that before the determination of nitrates was begun, some reaction had taken place. The nitrate may have been reduced to ammonia, and driven off when the water was boiled with sodium hydroxide. About 0.2 parts per million nitrites were found after four hours reduction in part VI, Table XII.

In order to show that some reaction had taken place in the waters of the two preceeding series, before the determinations were started, two other series of determinations were made.

The first, Table XIII, shows the results of the determination of nitrogen as nitrate on the three samples of water; and of a similar determination of some of the same waters to which 10 parts per million of N as nitrate had been added immediately before the analysis was made, By this method of proceedure, the chance for any reaction between the nitrates added and the impurities held in the water is greatly reduced. Under these conditions if the nitrate is completely reduced, the amounts found in the last part of Table XIII

TABLE XI.

TREATMENT OF SEWAGES AND POLLUTED WATERS.

Direct nesslerization, room temperature, four hours reduction.

Nitrates added 24 hours before analysis.						NH_3 in Traps.	
No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million.
I. Inflow at Urbana Septic Tank.							
1	100	200	50	0.5	0.20	.1	.01
2	100	200	50	0.5	0.20	.1	.01
3	100	200	50	0.4	0.16	.0	.00
II. Outflow at Urbana Septic Tank.							
1	100	200	50	0.4	0.16	.1	.01
2	100	200	50	0.5	0.20	.2	.02
3	100	200	50	0.6	0.24	.3	.03
III. Polluted Stream (Boneyard)							
1	100	200	50	2.4	0.96	.1	.01
2	100	200	50	2.5	1.00	.1	.01
3	100	200	50	2.6	1.04	.4	.04
IV. Same as I. + ten parts per million of nitrate.							
1	100	200	50	0.2	0.08	.0	.00
2	100	200	50	0.4	0.16	.8	.08
3	100	200	50	0.3	0.12	.2	.02
V. Same as II. + ten parts per million of nitrate.							
1	100	200	50	0.6	0.24	.2	.02
2	100	200	50	0.5	0.20	.0	.00
3	100	200	50	0.5	0.20	.3	.03
VI. Same as III + ten parts per million of nitrate.							
1	100	200	5	2.0	8.00	.5	.05
2	100	200	5	2.0	8.00	.7	.07
3	100	200	5	---	----	---	---

TABLE XII.

TREATMENT OF SEWAGES AND POLLUTED WATERS.

Direct nesslerization, room temperature, four hours reduction, nitrates added 24 hours before analysis.

No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	NH_3 in Traps. c.c. of Standard	Parts per Million.
I. Inflow at Urbana Septic Tank.							
1	100	200	50	0.4	0.16	.0	.0
2	100	200	50	0.3	0.12	.0	.0
3	100	200	50	0.4	0.16	.0	.0
II. Outflow at Urbana Septic Tank.							
1	100	200	50	0.4	0.16	.0	.0
2	100	200	50	0.3	0.12	.0	.0
3	100	200	50	0.2	0.08	.0	.0
III. Polluted Stream (Boneyard)							
1	100	200	25	3.7	2.96	.0	.0
2	100	200	25	3.8	3.04	.0	.0
3	100	200	25	3.7	2.96	.0	.0
IV. Same as I + ten parts per million of nitrate.							
1	100	200	50	0.8	0.32	.0	.0
2	100	200	50	0.4	0.16	.0	.0
3	100	200	50	0.5	0.20	.0	.0
V. Same as II + ten parts per million of nitrate.							
1	100	200	50	1.9	0.76	.0	.0
2	100	200	50	1.8	0.72	.0	.0
3	100	200	50	1.9	0.76	.0	.0
VI* Same as III + ten parts per million of nitrate.							
1	100	200	5	2.8	11.20	.0	.0
2	100	200	5	3.0	12.00	.0	.0
3	100	200	5	2.8	11.20	.0	.0

* Nitrites were found in the solution after four hours reduction. (about 0.2 parts per million)

TABLE XIII.

TREATMENT OF SEWAGES AND POLLUTED WATERS.

Direct nesslerization, room temperature, four hours reduction, nitrates added at time of analysis.

						NH_3 in Traps.	
No.	c.c. of Water	Vol. of Dilution	c.c. used	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million.
I. Inflow at Urbana Septic Tank.							
1	100	200	50	0.3	0.12	.0	.0
2	100	200	50	0.4	0.16	.0	.0
3	100	200	50	0.3	0.12	.0	.0
II. Outflow at Urbana Septic Tank.							
1	100	200	50	0.5	0.20	.0	.0
2	100	200	50	0.4	0.16	.0	.0
3	100	200	50	0.4	0.16	.0	.0
III. Polluted Stream (Boneyard)							
1	100	200	50	1.2	0.48	.0	.0
2	100	200	50	1.1	0.44	.0	.0
3	100	200	--	---	----	--	--
IV* Same as I + ten parts per million of nitrate.							
1	100	200	5	1.8	7.2	.0	.0
2	100	200	5	2.3	9.2	.0	.0
3	100	200	5	1.8	7.2	.0	.0
V* Same as II + ten parts per million of nitrate.							
1	100	200	5	2.3	9.2	.0	.0
2	100	200	5	2.5	10.0	.0	.0
3	100	200	5	2.3	9.2	.0	.0
*VI. Same as III + ten parts per million of nitrate.							
1	100	200	5	2.4	9.6	.2	.02
2	100	200	5	1.9	7.6	.0	.00
3	100	200	5	2.2	8.8	.0	.00

*Nitrites were found in the solution after four hours reduction.

should be equal to the amount of nitrates present in the original waters plus ten parts per million. In Table XIII, parts IV, V, and VI, where the results of the analyses of the samples to which ten parts per million of N as nitrate had been added, the results were a little lower than the theoretical. To account for the low results the remaining portions of the solutions were tested for nitrites. Nitrites were found to be present in all cases (see parts IV, V, VI, Table XIII) where nitrate had been added. This shows that the reduction is incomplete in four hours, and also shows that in sewages and polluted streams the reduction to ammonia is much slower.

The second series (Table XIV) shows the results of a determination of the free ammonia made on each of the three samples of water shown in Table XII before the nitrate was added, and also 24 hours after the nitrate had been added.

TABLE XIV.

DETERMINATION OF FREE AMMONIA IN THREE
SAMPLES OF WATER, TWO OF SEWAGE AND ONE POLLUTED STREAM
BEFORE AND 24 HOURS AFTER THE ADDITION OF NITRATES.

c.c. of Water	Vol. of Distillate	c.c. used	c.c. of Standard	Parts per Million	c.c. of Standard	Parts per Million.
Before the addition of the nitrates.					After addition of 10 parts per million Nitrates.)	
100	200	5	5.0	20.0	6.6	26.4
100	200	5	4.5	18.0	6.0	24.0
100	200	50	4.5	1.6	0.8	0.32

In the waters to which the nitrate had been added 24 hours before analysis there was found a much larger amount of ammonia than was originally present in the waters. This shows that part, at least, of the nitrate added had been reduced to ammonia, which in determining N as nitrates was driven off when the solution was boiled with sodium hydroxide. From a comparison of Table XII and Table XIV it is evident that nearly all of the nitrate lost had been converted into ammonia. The removal of nitrates by sewage and also the fact that sewages are free from N as nitrate would indicate that the determination of N as nitrate in sewage is without value.

CONCLUSIONS.

1. In the determination of ammonia after reduction, direct nesslerization may be successfully used in most waters. Distillation is to be preferred in the case of highly polluted streams and sewages.

2. The amount of ammonia obtained in a given time in open reduction tubes varies inversely with the temperature.

3. There is quite a large percent loss of ammonia during the reduction if the tubes are left open. But when traps are used practically all of the ammonia remains in solution, or, if carried out by the hydrogen, is reabsorbed by the solution in the reduction tube.

4. The reduction is completed in less than four hours in pure waters or waters of average purity.

5. In highly polluted waters and sewages we conclude that the determination of nitrates is valueless, first, because the amount usually found is practically zero. Second, because the impurities

present in such waters tend to remove any nitrate that may be present.

REFERENCES.

BRUCINE METHOD FOR NITRATES.

Zeit. Angew. Chem. 1894, 345.

Iowa Chemical Soc. (abs.) 1894, ii, 398.
G. Lunge & A. Lwoff

Chem. Zeit. 1899, 23, 454-55

Jour. Chem. Soc. (abs.) 1899, ii. 806.

Chem. Zeit. 1901, 25, 586.
L. W. Winkler.

Bull. Soc. Chem. 1901, iii, 25, 639.

Jour. Chem. Soc. (abs.) 1901, ii, 532.

Chem. Cents. 1900, ii, 878.

Pharm. Zeit. 45, 646.

Jour. Chem. Soc. (abs.) 1901, ii, 38

Zeit. Anal. Chem. 6, 71.

Jour. Chem. Soc. (abs.) 1902, 353

Zeit. Angew. Chem. 1902, 151-3; 170-172.
George Lunge.

Jour. Chem. Soc. (abs.) 1901, ii, 627.

Zeit. Angew. Chem. 1901, 14, 1317.

Jour. Chem. Soc. (abs.) 1902, 173.
Noll.

Z. Nahr. Genussm. 12, 53.

Abs. Jour. Amer. Chem. Soc. Jan. 20, 1907, 214.

REFERENCES TO ALUMINIUM REDUCTION METHOD FOR NITRATES.

Schulze,

Central Blatt. 42. p 186.

Zeit. fur Anal. Chem. Vol. 2, 305.

Ormandy and Cohn,

Jour. Chem. Soc. Vol. 57, p 811.

Hazen and Clark,

Chem. News. 1890, Vol. 62

Chem. News. 1891, Vol. 64, p 162.

Jour. Anal. & Applied Chem. June 1891.

Woy,

Zeit. öffentl. Chem. 1902, 8, 301.

Jour. Chem. Soc. (abs) 1902, ~~ii~~ 2, 694.